

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2004-146348

(43)Date of publication of application : 20.05.2004

(51)Int.Cl.

H01M 4/66
 H01M 2/16
 H01M 4/02
 H01M 4/04
 H01M 4/58
 H01M 4/60
 H01M 4/64
 H01M 10/36
 H01M 10/40

(21)Application number : 2003-164281

(71)Applicant : SAMSUNG SDI CO LTD

(22)Date of filing : 09.06.2003

(72)Inventor : LEE JAE-WOAN
CHO CHUNG-KUN

(30)Priority

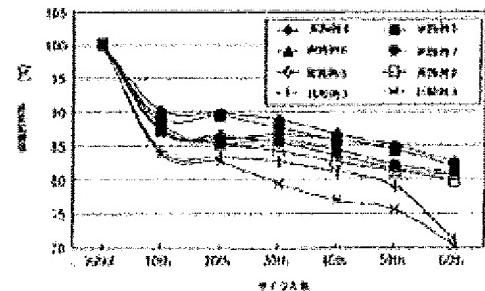
Priority number : 2002 200265483 Priority date : 25.10.2002 Priority country : KR

(54) NEGATIVE ELECTRODE FOR LITHIUM SECONDARY BATTERY, AND THE LITHIUM SECONDARY BATTERY CONTAINING SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a negative electrode for a lithium secondary battery having superior life time characteristics and a lithium secondary battery containing the same.

SOLUTION: The negative electrode for the lithium secondary battery contains a base material, having an average surface roughness of 30 Å to 4,000 Å and a lithium layer coated on the base material. The lithium secondary battery containing the negative electrode is superior in the life time characteristics.



* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]

A base material whose average surface roughness is 30A thru/or 4000A; it reaches.

A lithium layer coated on said base material;

An anode for ***** lithium secondary batteries.

[Claim 2]

The anode for lithium secondary batteries according to claim 1 whose average surface roughness of said base material is 30A thru/or 3000A.

[Claim 3]

The anode for lithium secondary batteries according to claim 2 whose average surface roughness of said base material is 30A thru/or 1500A.

[Claim 4]

The anode for lithium secondary batteries according to claim 3 whose average surface roughness of said base material is 30A thru/or 500A.

[Claim 5]

The anode for lithium secondary batteries according to claim 4 whose average surface roughness of said base material is 30A thru/or 100A.

[Claim 6]

The anode for lithium secondary batteries according to claim 1 in which said base material consists of conductive material.

[Claim 7]

The anode for lithium secondary batteries according to claim 1 chosen from a group which consists of a polymer film in which said base material was impregnated in metal foil, a metallic film, a conductive polymer film, a polymer film in which metal was vapor-deposited, and a conducting agent.

[Claim 8]

The anode for lithium secondary batteries according to claim 7 in which said metal is copper or nickel.

[Claim 9]

Said conductive polymer film Polyacetylene, polypyrrole, poly aniline, A polythiophene, poly (p-phenylene), poly (phenylenevinylene), A polyazulene (polyazulene), poly peri naphthalene (polyperinaphthalene), The anode for lithium secondary batteries according to claim 7 which is at least one chosen from a group which consists of poly acene (polyacene) and polynaphthalene-2,6-diyl.

[Claim 10]

Said metal a vapor-deposited polymer film Polyester, polyolefine, Polyamide, poly (vinylidene fluoride), poly (tetrafluoroethylene), Polystyrene, poly (acrylonitrile), poly (vinyl chloride), The anode for lithium secondary batteries according to claim 7 in which metal is vapor-deposited on at least one polymer film chosen from a group which consists of polycarbonate, polyacrylates and these copolymers, or these mixtures.

[Claim 11]

Said conducting agent a polymer film in which it was impregnated, Polyester, polyolefine, polyamide, poly (vinylidene fluoride), Poly (tetrafluoroethylene), polystyrene, poly (acrylonitrile), The anode for lithium secondary batteries according to claim 7 which is what a conducting agent is distributing in at least one polymer film chosen from a group which consists of poly (vinyl chloride), polycarbonate, polyacrylates and these copolymers, or these mixtures.

[Claim 12]

The anode for lithium secondary batteries according to claim 11 in which said conducting agent is chosen from a group which consists of a conductive metallic oxide, metal, and a carbon substance.

[Claim 13]

The anode for lithium secondary batteries according to claim 11 in which said conducting agent is chosen from a group which consists of tin oxide, phosphoric acid tin (SnPO_4), titanium oxide, a perovskite (perovskite) substance, tin, copper, nickel, black lead, and carbon black.

[Claim 14]

The anode for lithium secondary batteries according to claim 7 in which a polymer film in which said metal was vapor-deposited vapor-deposits metal on a polymer film whose average surface roughness is 30A thru/or 3000A.

[Claim 15]

The anode for lithium secondary batteries according to claim 7 whose average surface roughness of a polymer film in which

said metal was vapor-deposited is 30A thru/or 1500A.

[Claim 16]

The anode for lithium secondary batteries according to claim 7 whose average surface roughness of a polymer film in which said metal was vapor-deposited is 30A thru/or 500A.

[Claim 17]

The anode for lithium secondary batteries according to claim 7 whose average surface roughness of a polymer film in which said metal was vapor-deposited is 30A thru/or 100A.

[Claim 18]

The anode for lithium secondary batteries according to claim 1 which said lithium layer vapor-deposited lithium, and was formed on a base material, or is formed by sticking lithium foil by pressure.

[Claim 19]

A cathode containing at least one positive active material chosen from a group which consists of anode; by any 1 clause of the Claims 1-19 and a lithium contained metal oxide, a lithium content chalcogenide compound, a sulfur-systems substance, and conductive polymer;

A lithium secondary battery, ** and others.

[Claim 20]

The lithium secondary battery according to claim 19 which is that said lithium contained metal oxide or a lithium content chalcogenide compound is indicated to be by any one of the following chemical formulas :

$\text{Li}_x\text{Mn}_{1-y}\text{M}_y\text{A}_2$ (1)

$\text{Li}_x\text{Mn}_{1-y}\text{M}_y\text{O}_{2-z}\text{X}_z$ (2)

$\text{Li}_x\text{Mn}_2\text{O}_{4-z}\text{X}_z$ (3)

$\text{Li}_x\text{Mn}_{2-y}\text{M}_y\text{A}_4$ (4)

$\text{Li}_x\text{Co}_{1-y}\text{M}_y\text{A}_2$ (5)

$\text{Li}_x\text{Co}_{1-y}\text{O}_{2-z}\text{X}_z$ (6)

$\text{Li}_x\text{Ni}_{1-y}\text{M}_y\text{A}_2$ (7)

$\text{Li}_x\text{Ni}_{1-y}\text{O}_{2-z}\text{X}_z$ (8)

$\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_{2-z}\text{X}_z$ (9)

$\text{Li}_x\text{Ni}_{1-y-z}\text{Co}_y\text{M}_z\text{A}_{\alpha}$ (10)

$\text{Li}_x\text{Ni}_{1-y-z}\text{Co}_y\text{M}_z\text{O}_{2-\alpha}\text{X}_{\alpha}$ (11)

$\text{Li}_x\text{Ni}_{1-y-z}\text{Mn}_y\text{M}_z\text{A}_{\alpha}$ (12)

$\text{Li}_x\text{Ni}_{1-y-z}\text{Mn}_y\text{M}_z\text{O}_{2-\alpha}\text{X}_{\alpha}$ (13)

By said formula, it is $0.9 \leq x \leq 1.1$, $0 \leq y \leq 0.5$, $0 \leq z \leq 0.5$, and $0 \leq \alpha \leq 2$, M is at least one element chosen from a group which consists of aluminum, nickel, Co, Mn, Cr, Fe, Mg, Sr, V, or a rare earth element, A is the element chosen from a group which consists of O, F, S, and P, and X is F, S, or P.

[Claim 21]

Said sulfur-systems substance A sulfur element, Li_2S_n ($n \geq 1$), Li_2S_n dissolved in a catholyte (catholyte) ($n \geq 1$), The lithium secondary battery according to claim 19 chosen from a group which consists of an organosulfur compound, carbon, and sulfur polymer (C_2S_x) ($n: x = 2.5$ thru/or 50, $n \geq 2$).

[Claim 22]

Said lithium secondary battery contains a separator further between a cathode and an anode,

Said separator Polyethylene, polypropylene, polyvinylidene fluoride, The lithium secondary battery according to claim 19 chosen from a group which consists of polyethylene / polypropylene two-layer separator, polyethylene / polypropylene / three layers of polyethylene separator, and polypropylene / polyethylene / three layers of polypropylene separator.

[Claim 23]

The lithium secondary battery according to claim 19 in which said electrolyte of said lithium secondary battery is a non-aqueous electrolyte or a solid electrolyte including an electrolyte further.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]****[Field of the Invention]**

This invention relates to the lithium secondary battery containing the anode for lithium secondary batteries, and this, and relates to the lithium secondary battery which contains the anode for lithium secondary batteries and this excellent in the life characteristic in more detail.

[0002]**[Description of the Prior Art]**

Recently, in relation to the tendency of the miniaturization of a portable electronic device, and a weight saving, the necessity over highly-efficient-izing and large-scale-izing of the cell used as a power supply of these apparatus has been increasing. Such a cell generates electric power by using for a cathode and an anode the substance in which electrochemical reaction is possible. The element which influences the performance and the safety of a cell like the capacity of a cell, a life, and electric energy is the electrochemical characteristic of the active material which takes part in the electrochemical reaction of a cathode and an anode. Therefore, research which is going to improve the electrochemical characteristic of such a cathode or negative electrode active material is advanced.

[0003]

Among the active materials for cells used now, since the electric capacity per unit mass is large, lithium can provide a high capacity cell, and since electronegativity is large, it can provide a high-tension cell. Since a lithium metal is simultaneously used as an active material and a charge collector when using a lithium metal as negative electrode active material, it is not necessary to use a special current collector, and a lithium metal plate can be used as an anode polar plate as it is. What was manufactured by the method which vapor-deposits lithium by fixed thickness to metal, or has stuck lithium foil to sheets which are current collectors, such as metal foil or EKKUSUMETO (exmete;expanded metal), by pressure enough, and uses it as them can also be used as an anode polar plate. After vapor-depositing metal on a polymer film, lithium foil can be made to be able to adhere, or a lithium metal can be made to be able to vapor-deposit and can also be used.

[0004]

However, safety is lacking, a side reaction with the electrolysis solution of a lithium metal occurs easily, and since a dendrite is formed of this side reaction or the quantity of the lithium which increases also 4 times thru/or 5 times by positive-active-material contrast since it is long lasting is needed, a lithium metal has the difficulty on use. the anode polar plate manufactured with the above-mentioned vacuum evaporation or a crimping method -- lithium metal foil, although only lithium of the outside surface will take part in the electrochemical reaction of a cell most, At this time, when the surface state of a polar plate is not good, a dendrite will be formed remarkably and there is a problem that the quantity of the lithium which cannot take part in electrochemical reaction increases.

[0005]

Since the average surface roughness (R_a) of the vapor-deposited lithium is proportional to the average surface roughness of a base material when vapor-depositing lithium, a life characteristic falls rather than the lithium electrode in which the lithium electrode vapor-deposited using the base material with the coarse surface was vapor-deposited using the base material with the smooth surface. Since this has a phenomenon in which lithium electrodes gather previously at the spinode on the surface, etc. when a lithium ion moves by charge and discharge, When average surface roughness is coarse, dendrite formation of lithium becomes remarkable, and abundant generation of the lithium which cannot take part in a charge-and-discharge reaction any more eventually is carried out. Therefore, the life of a cell worsens rapidly.

[0006]

Therefore, by adjusting the average surface roughness of an anode base material in the desirable range, this invention person perceives the point that the life characteristic of a lithium secondary battery can be raised remarkably, and came to invent this invention.

[0007]**[Problem to be solved by the invention]**

It is for this invention solving the problem mentioned above, and the purpose of this invention is to provide the anode for lithium secondary batteries excellent in the life characteristic.

[0008]

The purpose of this invention is to provide the lithium secondary battery containing the anode excellent in said life characteristic.

[0009]

[Means for solving problem]

In order to attain said purpose, this invention provides the anode for lithium secondary batteries containing lithium layer; coated on base material; whose average surface roughness is 30A thru/or 4000A, and said base material.

[0010]

This invention provides again the lithium secondary battery containing said anode for lithium secondary batteries.

[0011]

[Mode for carrying out the invention]

Hereafter, with reference to the Drawings which attached this invention, it explains still in detail.

[0012]

According to the desirable working example 1 of this invention, the anode for lithium secondary batteries which can make the life characteristic of a lithium secondary battery improve remarkably can be provided. Drawing 1 shows the section of the anode for lithium secondary batteries of this invention.

[0013]

On the base material 20 whose average surface roughness is 30A thru/or 4000A, the lithium layer 30 is coated, the anode 10 for lithium secondary batteries of this invention is formed, and said base material is used as a current collector of an anode. As for the average surface roughness of said base material 20, 30A thru/or 3000 A are more preferred, 30A thru/or 1500 A are more preferred, it is more preferred that they are 30A thru/or 500A, and it is most preferred that they are 30A thru/or 100A. Since a labor and time are consumed too much as said average surface roughness is less than 30A, if economical efficiency is inferior and the average surface roughness of a base material exceeds 4000 A, Since the probability that lithium will gather at the spinode in the surface of an anode becomes high, the amount of dendrite formation of lithium increases, The generated amount of dead lithium (dead lithium) which cannot take part in a charge-and-discharge reaction any more increases, and there is a problem that the life characteristic of a cell worsens, so that charge and discharge progress.

[0014]

As for said anode base material 20, it is preferred that it is a conductive base material. Since the continuity of an electric network can be generated, it can continue and electronic supply can be received if a conductive base material is used, the quantity of the lithium which cannot take part in electrochemical reaction can be decreased.

[0015]

As such a conductive anode base material, metal foil, a metallic film, a conductive polymer film, the polymer film in which metal was vapor-deposited, the polymer film in which it was impregnated in the conducting agent, etc. can be used. Although the method of adjusting the average surface roughness of an anode base material changes with kinds of base material, when it is a metallic material, the polishing (polishing) method can be used, for example, and in being a polymer film, it purchases and uses the product which has the average surface roughness of said range.

[0016]

There is copper or nickel as metal usable as said metal foil or an anode base material of a metallic film form. As said conductive polymer film, polyacetylene, polypyrrole, Poly aniline, a polythiophene, poly (p-phenylene), poly (phenylenevinylene), There are a polyazulene (polyazulene), poly peri naphthalene (polyperinaphthalene), poly acene (polyacene), polynaphthalene-2,6-diyl, etc. The polymer film in which said metal was vapor-deposited means what vapor-deposited metal, such as copper or nickel, on the polymer film. Also as for the polymer film of the polymer film in which metal was vapor-deposited, since it has big influence on the average surface roughness of an anode base material, before metal is vapor-deposited, it is preferred to adjust average surface roughness in the same range as the average surface roughness of an anode base material. The polymer film in which it was impregnated in said conducting agent means the polymer film which the substance of a conductive metallic oxide, metal, or carbon is distributing in a polymer film. As a concrete example of said conducting agent, tin oxide, phosphoric acid tin (SnPO_4), There are titanium oxide and a conductive metallic oxide like a perovskite (perovskite) substance (LaSrO_3 , LaSrMnO_3), tin, copper and metal like nickel, black lead, carbon conductive material like carbon black, etc.

[0017]

As polymer used at the time of manufacture of the polymer film in which it was impregnated in the polymer film or conducting agent by which said metal was vapor-deposited, Polyester, such as poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT), Polyamide, such as polyolefines, such as polyethylene and polypropylene, and nylon, Poly (vinylidene fluoride), poly (tetrafluoroethylene), Polystyrene, poly (acrylonitrile), poly (vinyl chloride), Polyacrylates, such as polycarbonate and poly (methyl methacrylate), these copolymers, or these mixtures are used, and double poly (ethylene terephthalate), polypropylene, polyethylene, and poly (vinyl chloride) are used preferably.

[0018]

In the case of metal foil or a metallic film, the average surface roughness of an anode base material Rolling, It can adjust using methods, such as the polishing (polishing), when it is a polymer film, a coating disposal method can be used, and the polymer film which has the average surface roughness of the fixed range can also be purchased and used.

[0019]

If a lithium metal is coated and it uses as an anode on the base material excellent in average surface roughness, The probability that lithium ions will gather at any one spinode in the surface of a lithium electrode, etc. at the time of charge and discharge decreases, By this, formation of the dendrite of lithium can be controlled, the generated amount of dead lithium (dead lithium) which cannot take part in an electrochemical reaction any more at the time of charge and discharge can become less, and the life of a lithium secondary battery can be raised.

[0020]

In using for an anode the lithium metal which has a thickness of 50 micrometers or less, it usually uses the base material which can support an electrode, but if the base material with which average surface roughness was adjusted is used, since the average surface roughness of a lithium metal can also be adjusted in the desirable range, it is desirable.

[0021]

A deposition method is more preferred although the method etc. which vapor-deposit lithium, or have stuck lithium by pressure enough and make it the anode base material 20 on a base material as a method of forming the lithium layer 30 are used. The method of vapor-depositing lithium using a tungsten boat (Tungsten boat) or a molybdenum boat (Molybdenum boat) also in it is used most preferably. As for the pressure at the time of vacuum evaporation, it is preferred to be adjusted by the range of 5.0×10^{-7} torr thru/or 5.0×10^{-6} torr.

[0022]

Said lithium metal negative electrode can be used as an anode of a lithium secondary battery. A lithium secondary battery according to the kind of the separator and electrolyte to be used A lithium ion battery, It is classified into a lithium ion polymer battery and a lithium-polymer battery, is classified into a cylindrical shape, a square shape, a coin form, a pouch form, etc. according to a form, and can classify into a bulk type and a thin film type according to size. The structure and the manufacturing method of these cells are widely known for this field. The structure of the square-shaped lithium ion battery in this is shown in drawing 2. After said square-shaped lithium ion battery 3 puts the electrode group solid 4 containing the separator 7 which exists between the cathode 5, the anode 6 and said cathode 5, and the anode 6 into the case 8, it pours an electrolysis solution into the upper part of the case 8, and seals and assembles it with the cap plate 11.

[0023]

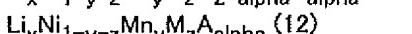
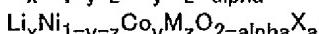
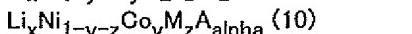
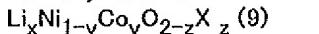
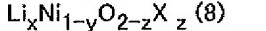
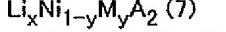
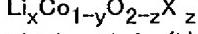
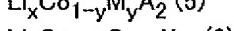
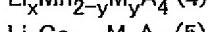
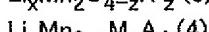
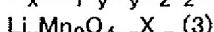
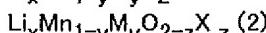
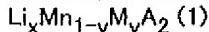
According to the desirable working example 2 of this invention, the lithium secondary battery containing the anode by said working example 1 is provided.

[0024]

Anode; and the lithium contained metal oxide in which said lithium secondary battery contains the lithium layer coated on the base material whose average surface roughness is 30A thru/or 4000A, and said base material, It consists of cathode; containing a lithium content chalcogenide compound, a sulfur-systems substance, and at least one positive active material chosen from the group which consists of conductive polymer.

[0025]

There is a compound as follows as a desirable example of the lithium contained metal oxide used as said positive active material, or a lithium content chalcogenide compound.



By said formula, it is $0.9 \leq x \leq 1.1$, $0 \leq y \leq 0.5$, $0 \leq z \leq 0.5$, and $0 \leq \alpha \leq 2$, M is at least one element chosen from the group which consists of aluminum, nickel, Co, Mn, Cr, Fe, Mg, Sr, V, or a rare earth element, A is the element chosen from the group which consists of O, F, S, and P, and X is F, S, or P.

[0026]

As a sulfur-systems substance used as said positive active material, There are a sulfur element, Li_2S_n ($n \geq 1$), Li_2S_n ($n \geq 1$) dissolved in the catholyte (catholyte), an organosulfur compound, carbon, sulfur polymer (C_2S_x) ($n \geq 2.5$ thru/or $n \geq 50$), etc.

[0027]

Depending on the kind of lithium secondary battery, a separator may exist between a cathode and an anode. As such a separator, polyethylene, polypropylene, polyvinylidene fluoride, or the multilayer film more than two-layer [these] is used. Of course, mixed multilayer films, such as polyethylene / polypropylene two-layer separator, polyethylene / polypropylene / three layers of polyethylene separator, polypropylene / polyethylene / three layers of polypropylene separator, are usable.

[0028]

As an electrolyte with which a lithium secondary battery is filled up, a non-aqueous electrolyte or a publicly known solid electrolyte is usable.

[0029]

Said non-aqueous electrolyte dissolves lithium salt in an organic solvent, and is manufactured. Carbonate, ester, ether, or ketone can be used for said organic solvent as a non-aqueous organic solvent. As said carbonate, dimethyl carbonate (DMC),

diethyl carbonate (DEC), Dipropyl carbonate (DPC), methylpropyl carbonate (MPC), Ethylpropyl carbonate (EPC), methylethyl carbonate (MEC), Can use ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), etc., and as said ester, n-methyl acetate, n-ethyl acetate, n-propyl acetate, etc. can be used, and wood ether (DME), a tetrahydrofuran (THF), etc. can be used as said ether.

[0030]

As said lithium salt, LiPF₆, LiBF₄, LiSbF₆, LiAsF₆, LiClO₄, LiCF₃SO₃, Li(CF₃SO₂)₂N, LiC₄F₉SO₃, LiAlO₄, LiAlCl₄, LiN(CxF_{2x+1}SO₂) (CyF_{2y+1}SO₂) (here) x and y mix one sort chosen from the group which consists of a certain LiCl and LiI, or two sorts or more, and are usable at a natural number.

[0031]

The polymer electrolyte which contains a polyethylene oxidation thing polymer electrolyte, one or more polyorganosiloxane side chains, or a polyoxyalkylene side chain as said solid electrolyte, Li₂S-SiS₂, Li₂S-GeS₂, Sulfur ghost electrolytes, such as Li₂S-P₂S₅ and Li₂S-B₂S₃, Inorganic compound electrolytes, such as Li₂S-SiS₂-Li₃PO₄ and Li₂S-SiS₂-Li₃SO₄, etc. are used preferably.

[0032]

Next, an working example desirable for an understanding of this invention is shown. However, it is not provided in order that the following working example may understand this invention more easily, and this invention is not necessarily restricted to the following working example.

[0033]

<Working example 1>

25-micrometer-thick copper foil was used as an anode base material. The average surface roughness of copper foil was measured using the optical 3D profiling system (optical 3D profiling system) (model name NT2000, WYKO manufacture). The measured average surface roughness (Ra) was 1400A (0.14 micrometer). The mask of the stainless-steel construction material as for which the square hole whose one side is 1.2 cm was vacant on copper foil was put, and the 1.5-micrometer-thick lithium metal was vapor-deposited. The test cell was manufactured using lithium foil as a counter electrode using as an anode the copper foil with which lithium was vapor-deposited. The electrolysis solution used for battery manufacturing is 1M. The dioxolane / jig lime / sulfolane / dimethoxyethane (volume ratio of 5/2/1/2) in which LiSO₃CF₃ was dissolved were used.

[0034]

<Working example 2>

What vapor-deposited copper was used for the poly (ethylene terephthalate) (PET) film as an anode base material. The tungsten boat was used for the 200-micrometer-thick PET film, copper was vapor-deposited by 2×10^{-6} torr, and the anode base material was manufactured. At this time, the thickness of the vapor-deposited copper was 0.1 micrometer, and the average surface roughness of the anode base material was 100A (0.01 micrometer). The average surface roughness of the anode base material was measured using the optical 3D profiling system (model name NT2000, WYKO manufacture). The mask of the stainless-steel construction material as for which the square hole whose one side is 1.2 cm was vacant on the anode base material was put, and the 1.5-micrometer-thick lithium metal was vapor-deposited. The test cell was manufactured using lithium foil as a counter electrode using this as an anode. The electrolysis solution used for battery manufacturing is 1M. The dioxolane / jig lime / sulfolane / dimethoxyethane (volume ratio of 5/2/1/2) in which LiSO₃CF₃ was dissolved were used.

[0035]

<Comparative example 1>

Except for average surface roughness having used the copper foil which is 4500A (0.45 micrometer) as an anode base material, the test cell was manufactured by the same method as said working example 1.

[0036]

Constant current charge and discharge were carried out for the test cell of said working examples 1 and 2 and the comparative example 1 for 360 seconds with the current density of 1 mA/cm², and cycle efficiency was measured. The result was indicated to the following table 1.

[Table 1]

	実施例 1	実施例 2	比較例 1
サイクル効率(%)	70.3%	80.7%	50.5%

[0037]

It turns out that cycle efficiency is superior to the comparative example 1 when using the anode of the working example 1 and the working example 2 which has the range of the average surface roughness of this invention, as shown in said table 1, and the cycle efficiency characteristic is excellent especially as average surface roughness is low.

[0038]

<Working example 3>

What vapor-deposited copper was used for the poly (ethylene terephthalate) (PET) film as an anode base material. The tungsten boat was used for the 200-micrometer-thick PET film, copper was vapor-deposited by 2×10^{-6} torr, and the anode

base material was manufactured. At this time, the thickness of the vapor-deposited copper was 0.1 micrometer, and the average surface roughness of the anode base material was 100A (0.01 micrometer). The average surface roughness of the anode base material was measured using the optical 3D profiling system (model name NT2000, WYKO manufacture). The mask of the stainless-steel construction material as for which the square hole whose one side is 1.2 cm was vacant on the anode base material was put, the 1.5-micrometer-thick lithium metal was vapor-deposited, and the anode was manufactured. [0039]

Reached sulfur powder as positive active material, polyethylene oxide (PEO) was reached as a binder, Ketchen black (ketjen black) was respectively reached 12weight % 75weight % as a conducting agent, it used 13weight %, and the cathode was manufactured. And the thickness of the separator was 16 micrometers, using 3 multistory porosity polymer film of polypropylene (PP) / polyethylene (PE) / polypropylene (PP) as a separator. The test cell was manufactured using said anode, the cathode, and the separator. The dimethoxyethane / jig lime / dioxolane (4:4:2 volume ratios) in which LiSO₃CF₃ of 1M was dissolved were used for the electrolyte used at the time of battery manufacturing.

[0040]

<Comparative example 2>

On the copper foil base material with a thickness of 10 micrometers which is 4470A (0.447 micrometer), average surface roughness vapor-deposited lithium 20micrometer, and manufactured the anode. The average surface roughness of the copper foil base material was measured using the optical 3D profiling system (model name NT2000, WYKO manufacture). Carrying out vacuum evaporation of lithium using the tungsten boat (Tungsten boat), the pressure at the time of vacuum evaporation was 2.0x10⁻⁶torr. The test cell was manufactured by the same method as the working example 3 using said anode.

[0041]

the test cell manufactured by said working example 3 and the comparative example 2 in order to check the effect which an anode base material gives to the life characteristic of a cell -- the voltage range of 1.5V thru/or 2.8V -- 0.2C charge -- and 0.5C discharge of was done, the life characteristic was evaluated, and the result was shown in drawing 3. Average surface roughness the life characteristic of the test cell of the working example 2 containing the anode in which lithium was vapor-deposited on the base material which is 100A as shown in drawing 3. It turns out that average surface roughness is dramatically superior to the test cell of the comparative example 2 containing the anode in which lithium was vapor-deposited on the base material which is 4470A.

[0042]

<The working examples 4-9 and the comparative examples 3-4>

In order to evaluate the battery characteristic by average surface roughness, respectively the average surface roughness of 200-micrometer-thick copper plates 450 A (working example 4), It adjusted to 1078 A (working example 5), 1424 A (working example 6), 2000 A (working example 7), 2473 A (working example 8), 3200 A (working example 9), 4537A (comparative example 3), and 5520 A (comparative example 4). On the copper plates in which average surface roughness was adjusted, 20 micrometers of lithium metals were vapor-deposited, and the anode was manufactured. Carrying out the deposition process using the tungsten boat, the pressure at the time of vacuum evaporation was 2x10⁻⁶torr. The test cell was manufactured by the same method as the working example 3 using the manufactured anode. The ratio of the capacity survival rate (remaining capacity/initial capacity) (x100) of a test cell was measured, and the result was indicated to the following table 2.

[0043]

[Table 2]

実施例及び比較例		10回目 残存率 (%)	20回目 残存率 (%)	30回目 残存率 (%)	40回目 残存率 (%)	50回目 残存率 (%)	60回目 残存率 (%)
実施例4	450Å	90.3	89.7	88.7	86.6	84.9	82.6
実施例5	1078Å	89.0	89.4	87.6	85.8	84.3	82.0
実施例6	1424Å	87.4	86.1	86.6	85.7	84.3	81.8
実施例7	2000Å	88.2	85.3	85.8	84.3	82.9	81.0
実施例8	2473Å	87.1	86.4	85.5	83.6	82.5	80.5
実施例9	3200Å	87.2	85.3	84.2	82.5	82.5	79.8
比較例3	4537Å	84.2	83.4	82.6	81.1	77.5	71.1
比較例4	5520Å	83.7	82.6	79.3	76.9	75.5	70.3

[0044]

The result of the data of said table 2 was shown in drawing 4. The life characteristic of the working example 4 thru/or the working example 9 which has average surface roughness in the range of this invention is excellent compared with the comparative example 3 and the comparative example 4 so that Table 2 and drawing 4 may show.

[0045]

[Effect of the Invention]

The anode for lithium secondary batteries of this invention can make the life characteristic of a lithium secondary battery improve by adjusting the average surface roughness of a base material in the fixed range compared with the existing lithium

metal negative electrode.

[0046]

Simple modification and change of this invention can be easily carried out by those who have the usual knowledge in this field, and it is considered that all of such modification or change are contained to the field of this invention.

[Brief Description of the Drawings]

[Drawing 1]It is a sectional view of the anode manufactured by this invention.

[Drawing 2]It is a sectional view of a lithium secondary battery.

[Drawing 3]It is the graph which showed the life characteristic of the test cell of the working example 3 and the comparative example 2.

[Drawing 4]It is the graph which showed the life characteristic of the test cell of the working example 4 thru/or the working example 9 and the comparative example 3 thru/or the comparative example 4.

[Explanations of letters or numerals]

3 Cell

4 Electrode group solid

5 Cathode

6 Anode

7 Separator

8 Case

10 Lithium metal negative electrode

11 Cap plate

20 Base material

30 Lithium layer

[Translation done.]